

CATALYTIC COMPOSITION FOR THE UPGRADING OF HYDROCARBON MIX-
TURES

10 The present invention relates to a catalytic composi-
tion which comprises a beta zeolite, a metal of group VIII,
a metal of group VI B and optionally one or more oxides as
carrier. The catalytic system of the present invention can
be used for the hydrotreating of hydrocarbon mixtures and
more specifically for the upgrading of hydrocarbon mixtures
15 which boil within the naphtha range, containing sulfur im-
purities, i.e. in the hydrodesulfuration with contempora-
neous skeleton isomerization and a reduced hydrogenation
degree of the olefins contained in said hydrocarbons, the
whole process being carried out in a single step. This
20 catalytic system can be used, in particular, for the up-
grading of mixtures of hydrocarbons which boil within the
naphtha range deriving from cracking processes, preferably
mixtures of hydrocarbons having a boiling point within the
naphtha range deriving from FCC catalytic cracking (Fluid
25 Catalytic Cracking).

Hydrocarbons which boil within the naphtha range deriving from FCC (i.e. gasoline cut) are used as blending component of gasolines. For this purpose, it is necessary for them to have a high octane number together with a low sulfur content, to conform with the law restrictions which are becoming more and more severe, in order to reduce the emission of contaminants. The sulfur present in gasoline mixtures in fact mainly comes (>90%) from the gasoline cut deriving from FCC.

This cut is also rich in olefins which have a high octane number. Hydrogenation processes used for desulfuration also hydrogenate the olefins present with a consequent considerable reduction in the octane number (RON and MON). The necessity has therefore been felt for finding a catalytic system which decreases the sulfur content in hydrocarbon mixtures which boil within the naphtha range and, at the same time, minimizes the octane loss (RON and MON), which can be achieved, for example, by the skeleton isomerization of the olefins present and/or by inhibiting the hydrogenation of the olefinic double bond.

The use of zeolites with a medium pore dimension as isomerization catalysts and the consequent recovery of octane in the charges already subjected to desulfuration are already known (US 5,298,150, US 5,320,742, US 5,326,462, US 5,318,690, US 5,360,532, US 5,500,108, US 5,510,016, US

5,554,274, US 599,439). In these known processes, in order to obtain hydrodesulfuration with a reduced octane loss, it is necessary to operate in two steps, using in the first step catalysts suitable for desulfuration and in the second
5 step catalysts for recovering the octane number.

US 5.378.352 describes a process in a single step for desulfurating hydrocarbon fractions, with boiling points within the range of gasolines, using a catalyst which comprises a metal of group VIII, a metal of group VI, a zeo-
10 lite selected from ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, MCM-22 and mordenite, and a metal oxide as ligand, with a process temperature preferably higher than 340°C.

Some catalytic materials containing metals of group
15 VIII and group VI B, a refractory carrier and a zeolite selected from ZSM-35, ZSM-5, mordenite and fujasite, are described in EP 442159, EP 437877, EP 434123 for the isomerization and disproportioning of olefins; in US 4343692 for hydrodewaxing; in US 4519900 for hydrodenitrogenation, in
20 EP 072220 for a process in two steps comprising dewaxing and hydrodesulfuration; in US 4959140 for a hydrocracking process in two steps.

We have now surprisingly found a new catalytic system which can be used for the hydrotreating of hydrocarbon mix-
25 tures and, more specifically, we have found a catalytic

system with which it is possible to desulfurate, with high conversion values, mixtures of hydrocarbons that boil within the naphtha range containing sulfur and olefins and contemporaneously obtain the skeleton isomerization of the olefins present with a low hydrogenation degree of the olefinic double bond. This new catalytic system is also active at temperatures and pressures that are lower than those preferably used in the known art for desulfuration.

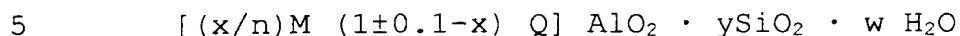
Both skeleton isomerization and reduced olefinic hydrogenation enable hydrocarbon mixtures to be obtained, which boil within the naphtha range with very low RON (research octane number) and MON (motor octane number) losses.

The catalytic compositions of the present invention can not only be used for the desulfuration of hydrocarbon cuts that boil within the "heavy naphtha" range (130°-250°C), i.e. cuts poor in olefins, but also feeds of "full range naphtha", which boil within the range of 35°-250°C, i.e. in the case of cuts rich in olefins. In fact, the catalytic system of the present invention has a high selectivity for desulfuration with respect to hydrogenation, which represents an additional advantage in terms of octane recovery in the end-gasoline.

A first object of the present invention therefore relates to a catalytic composition which comprises a beta zeolite, a metal of group VIII, a metal of group VI B, and

optionally one or more oxides as carrier.

Beta zeolite is a porous crystalline material described in US 3,308,069, having a molar composition of oxides corresponding to the following formula:



wherein x is less than 1, preferably less than 0.75, y varies within the range of 5 to 100, w varies within the range of 0 to 4, M is a metal selected from metals of groups IA, IIA, IIIA, or is a transition metal, n is the valence of M
10 and Q is a hydrogen ion, ammonium ion, an organic cation or a mixture of these. Preferably y is greater than 5 and less than 50.

According to a particularly preferred aspect of the present invention the beta zeolite is in acid form i.e. in
15 the form in which the cationic sites of the zeolite are prevalently occupied by hydrogen ions. It is especially preferable for at least 80% of the cationic sites to be occupied by hydrogen ions.

According to an aspect of the present invention, when
20 the catalytic composition comprises beta zeolite and metals of group VIII and group VI B, said zeolite is preferably present in a quantity ranging from 70 to 90%; when the catalytic composition also comprises one or more oxides as carrier, said zeolite is preferably present in a quantity
25 ranging from 5 to 30% by weight with respect to the total

weight of the catalyst.

The catalysts used in the present invention preferably contain Cobalt or Nickel as metal of group VIII, whereas the metal of group VI B is preferably selected from molybdenum or tungsten. According to a particularly preferred aspect, Co and Mo are used. The weight percentage of the metal of group VIII preferably varies from 1 to 10% with respect to the total weight of the catalyst, even more preferably from 2 to 6%; the weight percentage of the metal of group VI B preferably varies from 4 to 20% with respect to the total weight of the catalyst, even more preferably from 7 to 13%. The weight percentages of the metal of group VI B and the metal of group VIII refer to the content of metals expressed as metal element of group VI B and metal element of group VIII; in the end-catalyst the metals of group VI B and VIII are in the form of oxides. According to a particularly preferred aspect, the molar ratio between the metal of Group VIII and the metal of group VI B is less than or equal to 2, preferably less than or equal to 1.

The oxide used as carrier is preferably the oxide of an element Z selected from silicon, aluminum, titanium, zirconium and mixtures of these. The carrier of the catalytic composition can consist of one or more oxides and the oxide used is preferably alumina or alumina mixed with an oxide selected from silica and zirconia.

salt of the metal of group VI B and, optionally, tetra-alkylammonium hydroxide having the formula R_4NOH ;

5 d) aging of the gel at a temperature ranging from 10 to
40°C;

f) calcination of the gel.

In step a) of this preparation, the metal salt of group VIII is, for example, a nitrate, a hydroxide, an acetate, an oxalate, and preferably a nitrate.

15 The organic compound capable of generating the sup-
porting oxide or oxides, by means of hydrolysis and subse-
quent gelations and calcination, is preferably the corre-
sponding alkoxide or alkoxides, in which the alkoxide sub-
stituents have the formula $(R'O)-$ wherein R' is an alkyl
20 containing from 2 to 6 carbon atoms. The alkoxide is pref-
erably an element Z selected from silicon, aluminum, tita-
nium, zirconium and their mixtures; in particular, when Z
is aluminum, it is a trialkoxide having the formula
 $(R'O)_3Al$, wherein R' is preferably an isopropyl or a sec-
25 butyl; when Z is silicon, it is a tetraalkoxide having the

formula $(R'O)_4Si$ wherein R' is preferably ethyl and, when Z is Zr , it is an alkoxide having the formula $(R'O)_4Zr$ wherein R' is preferably isopropyl.

In step b) the soluble salt of the metal of group VI B
5 can be an acetate, an oxalate or ammonium salts, and is preferably an ammonium salt. The tetraalkylammonium hydroxide has the formula R_4NOH wherein R is an alkyl group containing from 2 to 7 carbon atoms. According to a preferred aspect the solution in step b) also contains formamide
10 (Drying Control Chemical Agent) which favours the stabilization of the porous structure during the drying phase.

The quantities of the reagents are selected in relation to the composition of the end-catalyst.

In step c), according to the preferred sequence, the
15 solution of step b) is added to the suspension of step a).

In step d) the gel obtained is maintained at a temperature ranging from 10 to 40°C, for a time of 15-25 hours.

Step e) is carried out at a temperature ranging from
20 80 to 120°C.

Step f) is carried out at a temperature ranging from 400 to 600°C.

According to another aspect of the present invention, the catalytic system containing one or more oxides as carrier
25 rier can be prepared as follows:

a) an alcoholic dispersion is prepared, containing beta zeolite and one or more organic compounds capable of generating the supporting oxide or oxides;

b) an aqueous solution is prepared containing tetra-
5 alkylammonium hydroxide having the formula R_4NOH ;

c) the alcoholic dispersion and the aqueous dispersion are mixed and a gel is obtained;

d) aging of the gel at a temperature ranging from 10 to 40°C;

10 e) drying of the gel;

f) calcination of the gel;

g) impregnation of the calcined product with a solution containing a salt of a metal of group VI B, drying, calcination and impregnation with a solution of a salt of a
15 metal of group VIII, drying and calcination.

The quantities of the reagents are selected in relation to the composition of the end-catalyst. The reagents used are the same as the sol-gel synthesis.

According to another aspect of the present invention,
20 the catalytic compositions containing the supporting oxide or oxides can be prepared as follows:

a) an alcoholic dispersion is prepared, containing a soluble salt of the metal of group VIII and one or more organic compounds capable of generating the supporting oxide or ox-
25 ides;

b) an aqueous solution is prepared containing a soluble salt of the metal of group VI B and, optionally, tetra-alkylammonium hydroxide having the formula R_4NOH ;

c) the alcoholic dispersion and the aqueous dispersion are
5 mixed and a gel is obtained;

d) aging of the gel at a temperature ranging from 10 to 40°C;

e) drying of the gel;

f) mechanical mixing of the dried product with beta zeo-
10 lite;

g) calcination.

The reagents used are the same as the sol-gel synthesis.

The quantities of the reagents are selected in relation to the composition of the end-catalyst.
15

According to another aspect of the present invention, the catalytic compositions containing one or more oxides as carrier can be prepared as follows:

a) impregnation of the carrier, consisting of one or more
20 oxides, with a salt of a metal of group VI B and with a salt of a metal of group VIII,

b) drying and calcination of the material obtained in step a),

c) mixing of the impregnated oxide obtained in step b) with
25 the beta zeolite.

tionally a ligand of the pseudoboehmite type, added to the catalyst to form a paste which can be extruded. In particular, when the catalysts are prepared by sol-gel, the addition of the ligand is not necessary during the extrusion
5 process.

The materials of the present invention can be used as catalysts for the hydrotreating of hydrocarbon mixtures and more specifically for the upgrading of hydrocarbon mixtures which boil within the naphtha range.

10 A further object of the present invention therefore relates to the hydrotreating of hydrocarbon mixtures characterized by the use of a catalytic composition which comprises a beta zeolite, a metal of group VIII, a metal of group VI B, and optionally one or more oxides as carrier.

15 In accordance with this, a particularly preferred aspect of the present invention relates to the hydrodesulfuration of hydrocarbon mixture having boiling ranges within the range of about 35° to about 250°C, containing olefins and at least 150 ppm of sulfur, with the contemporaneous
20 skeleton isomerization of these olefins, which comprises putting these mixtures in contact, in the presence of hydrogen, with a catalytic composition which comprises a beta zeolite, a metal of group VIII, a metal of group VI B, and optionally one or more oxides as carrier.

25 When the catalytic composition containing the beta zeolite,

5 tivated, before use, by sulfidation according to the known
methods. According to a particular aspect of the present
invention, it is possible to effect the desulfuration and
isomerization process in a reactor in which the catalytic
composition is divided into two beds, the first containing
the beta zeolite, the second containing the remaining
catalytic component containing a metal of group VI B, a
metal of group VIII and one or more oxides as carrier.

EXAMPLE 1 - Preparation of catalyst A

10 1.17 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (CoN) are dissolved in 53.32 g
of BuOH, at room temperature. 0.79 g of beta zeolite (in
acid form, with a ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 26.3$, prepared in ac-
cordance with US 3,308,069) are added, which are suspended
in the alcoholic solution, heating to 60°C for 10 minutes.
15 30.33 g of $\text{Al}(\text{OC}_4\text{H}_9)_3$ (aluminum sec-butoxide) are added to
this suspension which is heated to 60°C for 20 minutes, ob-
taining the suspension A1.

20 1.66 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (ammonium heptamolybdate,
EMA) are dissolved in 19.60 g of $(\text{C}_3\text{H}_7)_4\text{NOH}$ (tetra-propyl
ammonium-hydroxide, TPAOH, solution at 19.2%), at room tem-
perature, obtaining the solution A2 (pH = 10).

25 Solution A2) is slowly poured into the suspension A1), un-
der heating and under stirring, obtaining a highly viscous
fluid which is maintained at 80°C for 1 hour. This is fol-
lowed by aging at room temperature for 21 hours, drying in

EXAMPLE 3 - Preparation of catalyst C (comparative)

A comparative catalyst is prepared as described in EP 748652. 1.04 g of CoN are dissolved in 47.16 g of BuOH, at room temperature. 1.03 g of $\text{Si}(\text{OC}_2\text{H}_5)_4$ (Tetraethyl-
5 orthosilicate) and 26.53 g of $\text{Al}(\text{OC}_4\text{H}_9)_3$ (aluminum sec-butoxide) are added and the mixture is heated to 60°C for 10 minutes, obtaining the suspension C1.

1.47 g of EMA are dissolved in 17.56 g of TPAOH (solution at 19.2%), at room temperature, obtaining the solution
10 C2, (pH = 11).

The solution C2) is slowly poured into the suspension C1), under heating and under stirring, obtaining a highly viscous fluid which is maintained at 60°C, for 1 hour. This is followed by aging at room temperature for 21 hours,
15 drying in a vacuum oven at 100°C for 6 hours, and calcination in muffle under the same conditions as in example 1. The characteristics of the material are indicated in Table 1.

EXAMPLE 4 - Preparation of catalyst D (comparative)

20 A comparative catalyst is prepared as described in EP 748652. 3.30 g of CoN are dissolved in 47.48 g of BuOH, the temperature being maintained at 60°C for 15 minutes. 1.00 g of $\text{Si}(\text{OC}_2\text{H}_5)_4$ (Tetraethyl-orthosilicate) and 25.10 g of $\text{Al}(\text{OC}_4\text{H}_9)_3$ (aluminum sec-butoxide) are added and the mixture
25 is heated to 60°C for 15 minutes, obtaining the suspension

D1.

3.20 g of EMA are dissolved in 33.00 g of TPAOH (solution at 19.2%), at room temperature, obtaining the solution D2, (pH = 11).

5 The solution D2) is slowly poured into the suspension D1), under heating and under stirring, obtaining a highly viscous fluid which is maintained at 60°C, for 1 hour. This is followed by aging at room temperature for 16 hours, drying in a vacuum oven at 100°C for 6 hours, and calcination in muffle under the same conditions as example 1. The characteristics of the material are indicated in Table 1.

EXAMPLE 5 - Preparation of catalyst E (comparative)

1.18 g of CoN are dissolved in 36.17 g of BuOH at room temperature. 0.63 g of commercial ZSM-5 zeolite (PQ 3070E) are added, and are suspended in the alcohol solution, heating to 50°C, for 10 minutes. 30.11 g of $\text{Al}(\text{OC}_4\text{H}_9)_3$ (aluminum sec-butoxide) are added to this suspension and the mixture is heated to 60°C for 20 minutes, obtaining the suspension E1.

20 1.67 g of EMA are dissolved in 19.41 g of TPAOH (solution at 19.2%), at room temperature, obtaining the solution E2, (pH = 10).

The solution E2) is slowly poured into the suspension E1), under heating and under stirring, obtaining a highly viscous fluid which is maintained at 80°C, for 1 hour.

This is followed by aging at room temperature for 22 hours, drying in a vacuum oven at 100°C for 6 hours, and calcination in muffle with the temperature program indicated in example 1. The characteristics of the material are indicated in Table 1.

EXAMPLE 6 - Catalyst F (comparative)

A reference commercial catalyst is used consisting of a system based on alumina, cobalt and molybdenum. The characteristics of this catalyst are indicated in Table 1

TABLE 1

Catalyst	Zeolite (w%)	Co (w%)	Mo (w%)	Co/Mo (mol)	A _{surf} (m ² /g)	V _{pores} (cm ³ /g)
A	9.0 beta	2.2	8.1	0.44	380	1.10
B	19.6 beta	2.5	8.2	0.49	465	1.24
C	--	2.3	8.9	0.42	360	0.74
D	--	6.8	18.1	0.61	430	0.72
E	7.4 ZSM-5	2.8	10.5	0.45	410	1.05
F	--	3.2	12.0	0.43	245	0.51

CATALYTIC TESTS ON MODEL CHARGE

The catalytic results obtained by treating a feed, defined as model charge, representative of the composition of an FCC gasoline in terms of S content and olefinic cut, are provided hereunder. The model charge has the following composition:

- 30% by weight of 1-pentene;
- 0.25% by weight of thiophene (1000 ppm S);

EXAMPLE 8: Catalytic activity of catalyst D

2 g of catalyst D are treated as in example 6 as regards the activation procedure and then tested on the model charge under the operating conditions described in Table 2, which also indicates the catalytic results.

EXAMPLE 9: Catalytic activity of catalyst E

2 g of catalyst E are treated as in example 6 as regards the activation procedure and then tested on the model charge under the operating conditions described in Table 2, which also indicates the catalytic results.

EXAMPLE 10: Catalytic activity of catalyst F

2 g of catalyst F are treated as in example 6 as regards the activation procedure and then tested on the model charge under the operating conditions described in Table 2, which also indicates the catalytic results.

TABLE 2

CATALYST	T (°C)	WHSV (hrs ⁻¹)	HDS (%)	ISO (%)	HDS/HYD	HYD/ISO
A	256	4.3	84.1	15.5	2.1	2.6
A	295	10.0	96.9	14.7	1.7	3.9
C	254	6.6	91.0	2.5	1.2	29.9
C	282	6.6	92.7	2.5	0.9	40.4
D	273	3.9	88.0	0.7	1.0	120.95
D	290	3.9	95.0	0.7	1.05	127.9
E	254	3.3	40.3	13.3	0.7	4.5
F	250	4.0	89.7	2.5	2.4	15.0

The catalyst of the present invention (A) increases the isomerizing activity by about one order of magnitude, with respect to those without zeolite, regardless of the

- the complement to 100 is n-hexane.

The catalysts are all activated following the same procedure, in a stream of H_2S/H_2 .

The catalytic activity is evaluated using the following parameters:

a) hydrodesulfuration conversion (HDS %), calculated as follows:

$$\text{HDS \%} = 100 \times (\text{ppm } S_{in} - \text{ppm } S_{out}) / \text{ppm } S_{in}$$

b) isomerizing properties ISO % calculated as follows:

$$\text{ISO \%} = 100 \times (\text{i-pentanes} + \text{i-pentenenes}) / \Sigma C_5$$

c) hydrogenating property HYD % calculated as follows:

$$\text{HYD \%} = 100 \times (\text{n-pentane}_{out} / \text{1-pentene}_{in})$$

EXAMPLE 6: Catalytic activity of catalyst A

2 g of catalyst A, diluted with corundum, are charged into a reactor (40-70 mesh) and activated in the presence of H_2S/H_2 (10% vol) up to 400°C for 3 hours; the system is then brought under H_2 pressure up to 10 bars and the model feed is sent, with a ratio H_2 /hydrocarbon charge equal to 300 Nl/l. The operating conditions and catalytic results are indicated in Table 2.

EXAMPLE 7: Catalytic activity of catalyst B

2 g of catalyst B are treated as in example 6 as regards the activation procedure and then tested on the model charge under the operating conditions described in Table 2, which also indicates the catalytic results.

fact that the metal content is the same, as in catalyst C, or double, as in catalyst D. This is also observed with respect to the commercial catalyst F.

The presence of beta zeolite increases the HDS conversion with respect to the HYD hydrogenating properties, as is demonstrated by the higher value of the HDS/HYD ratio and also reduces hydrogenation with respect to isomerization (lower value of the HYD/ISO ratio), with respect to both the compositions without zeolite (C and D) and to the catalyst with ZSM-5 zeolite (E).

In addition the catalyst of the present invention also reaches a high HDS at a bland temperature ($T=256^{\circ}\text{C}$) and in particular is double with respect to the catalyst E, containing ZSM-5.

The high values for the HDS/HYD ratio and low values for the HYD/ISO ratio (i.e. high desulfuration with a reduced hydrogenating activity and high skeleton isomerization) show how the catalysts of the present invention are capable of recovering the octane loss in hydrocarbon mixtures which are subjected to hydrosulfuration, having boiling ranges within the range of 35° to 250°C , containing olefins and at least 150 ppm of sulfur.